

English Translation of JP-A-8-59818

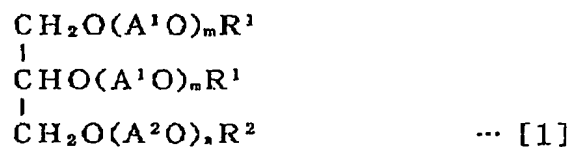
[Title of the Invention]

GLYCERIN POLYALKYLENE GLYCOL ETHER DERIVATIVE

[Abstract]

[Constitution]

A glycerin polyalkylene glycol ether derivative represented by the formula [1]:



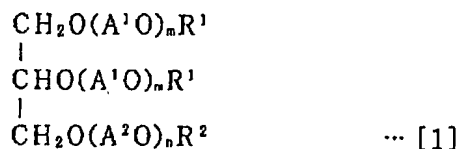
wherein $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products thereof; $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are different in structure from each other; R^1 and R^2 are each a hydrogen atom or a hydrocarbon group or acyl group having 1 to 24 carbon atoms and may be the same or different; m is from 1 to 200; and n is from 1 to 200.

[Advantages]

The glycerin polyalkylene glycol ether derivative of the present invention is different in physical properties from those having all the same polyalkylene chains, and can be utilized as a novel surfactant.

[Claims]

[Claim 1] A glycerin polyalkylene glycol ether derivative represented by the general formula [1]:



wherein A^1O and A^2O are each an oxyalkylene group having 2 to 4 carbon atoms; $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products thereof; $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are different in structure from each other; R^1 and R^2 are each a hydrogen atom or a hydrocarbon group or acyl group having 1 to 24 carbon atoms and may be the same or different; m and n mean each an added mole number of an alkylene oxide; m is from 1 to 200; and n is from 1 to 200.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a glycerin polyalkylene glycol ether derivative. More specifically, it relates to a novel glycerin polyalkylene glycol ether derivative having polyoxyalkylene chains different in

composition between α -, β -positions and γ -position of the glycerin residue.

[0002]

[Prior Art]

It is known that a polyalkylene glycol ether of glycerin is synthesized by adding an alkylene oxide to glycerin. It is known that such a polyalkylene glycol ether of glycerin and further etherified or esterified compounds thereof are useful as surfactants, lubricants, cosmetics, or defoaming agents. However, polyalkylene glycol ethers of glycerin hitherto synthesized are compounds wherein alkylene oxides having the same composition are added to three hydroxyl groups at α -, β -, and γ -positions of glycerin at the same time, and hence three polyoxyalkylene chains have the same structure both in composition and chain length. As compounds different in structure at α -, β -, and γ -positions of glycerin, JP-A-64-13046 and JP-A-6-145341 disclose glycerin derivatives wherein an alkylene oxide is added only to α -position of a glycerin residue. Hitherto, it is easy to synthesize a glycerin derivative having polyoxyalkylene chains of the same structure at α -, β -, and γ -positions of glycerin by adding an alkylene oxide to glycerin but a glycerin derivative having polyoxyalkylene chains different in composition at α -, β -, and γ -positions of glycerin is not

known and it is desired to develop such a glycerin polyalkylene glycol ether derivative.

[0003]

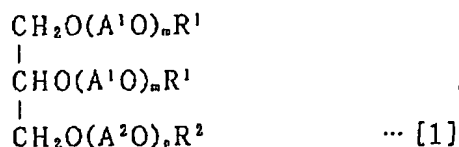
[Problems that the Invention is to Solve]

The present invention is accomplished for the purpose of providing a glycerin polyalkylene glycol ether derivative having polyoxyalkylene chains different in composition between α -, β -positions and γ -position of the glycerin residue.

[0004]

[Means for Solving the problems]

As a result of extensive studies for solving the above problems, the present inventors have found that a compound wherein polyoxyalkylene chains different in structure are added to three hydroxyl groups of glycerin is obtained by protecting one or two hydroxyl groups of glycerin through etherification, esterification, or the like, adding an alkylene oxide to remaining hydroxyl group(s), converting the protected hydroxyl group(s) into free hydroxyl group(s), and further adding an alkylene oxide. Thus, based on this finding, they have accomplished the invention. Namely, the invention provides a glycerin polyalkylene glycol ether derivative represented by the general formula [1]:



wherein A^1O and A^2O are each an oxyalkylene group having 2 to 4 carbon atoms; $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products thereof; $(\text{A}^1\text{O})_m$ and $(\text{A}^2\text{O})_n$ are different in structure from each other; R^1 and R^2 are each a hydrogen atom or a hydrocarbon group or acyl group having 1 to 24 carbon atoms and may be the same or different; m and n mean each an added mole number of an alkylene oxide added; m is from 1 to 200; and n is from 1 to 200.

[0005]

In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], the oxyalkylene group having 2 to 4 carbon atoms represented by A^1O and A^2O includes an oxyethylene group, an oxypropylene group, an oxybutylene group, an oxytetramethylene group, and the like. They can be formed by adding ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, and the like. These compounds may be added singly or in combination of two or more of them. In

the case that two or more of them are added, the derivative may be a random form or a block form. In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], $(A^1O)_m$ and $(A^2O)_n$ are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products, and $(A^1O)_m$ and $(A^2O)_n$ are different in structure from each other. The fact that $(A^1O)_m$ and $(A^2O)_n$ are different in structure from each other means that the compositions constituting $(A^1O)_m$ and $(A^2O)_n$ are different from each other, the combining modes of the oxyalkylene groups constituting $(A^1O)_m$ and $(A^2O)_n$ are different from each other, for example, one is a random form and another is a block form, the chain lengths of polyoxyalkylene chains are different in $(A^1O)_m$ and $(A^2O)_n$, and the like. In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], the structures of the polyoxyalkylene chains combined with three hydroxyl groups of glycerin are different between the polyoxyalkylene chains combined at α - and β -positions and the polyoxyalkylene chain combined at γ -position and also the chain lengths of respective chain parts and hydrophilicity-lipophilicity balance possessed by respective chain parts can be independently

changed, so that properties as a surfactant can be optionally adjusted. Such a surfactant is useful as a raw material or a basal material for lubricants, cosmetics, and pharmaceuticals and as a defoaming agent. In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], m and n mean each an added mole number of an alkylene oxide, and m is from 1 to 200, preferably from 5 to 100, more preferably from 10 to 80 and n is from 1 to 200, preferably from 5 to 100, more preferably from 10 to 80. When m or n exceeds 200, viscosity of the glycerin polyalkylene glycol ether derivative becomes high. In the invention, the derivatives including cases wherein m is 1 and n is 1 are generally called as glycerin polyalkylene glycol ether derivatives.

[0006]

In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], the hydrocarbon group having 1 to 24 carbon atoms represented by R^1 and R^2 includes linear or branched, saturated or unsaturated aliphatic hydrocarbon groups, alicyclic hydrocarbon groups, aromatic hydrocarbon groups, and the like. Examples of such a hydrocarbon group include a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a sec-

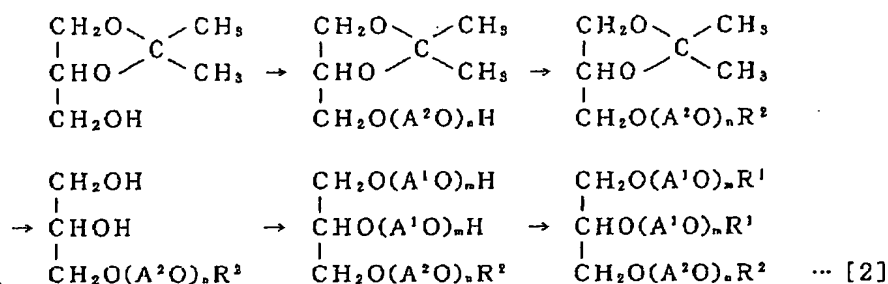
butyl group, a tert-butyl group, a pentyl group, an isopentyl group, a neopentyl group, a tert-pentyl group, a hexyl group, a heptyl group, a 2-ethylhexyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a hexadecyl group, an isocetyl group, an octadecyl group, an isostearyl group, an oleyl group, an icosyl group, a docosyl group, a tetracosyl group, a benzyl group, a cresyl group, a butylphenyl group, a dibutylphenyl group, an octylphenyl group, a nonylphenyl group, a dodecylphenyl group, a dioctylphenyl group, dinonylphenyl group, a styrenated phenyl group, and the like. The carbon number of the hydrocarbon group represented by R^1 and R^2 is from 1 to 24, preferably from 1 to 12, more preferably from 1 to 4. When the carbon number of the hydrocarbon group represented by R^1 and R^2 exceeds 24, the reaction becomes difficult to occur. In the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], examples of the acyl group having 1 to 24 carbon atoms represented by R^1 and R^2 includes acyl groups derived from formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, caproic acid, caprylic acid, 2-ethylhexanoic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, isopalmitic acid, margarine acid, stearic acid, isostearic

acid, arachidic acid, behenic acid, acrylic acid, methacrylic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, benzoic acid, and the like. The carbon number of the acyl group represented by R^1 and R^2 is from 1 to 24, preferably from 2 to 18, more preferably 2 and from 12 to 18. When the carbon number of the acyl group represented by R^1 and R^2 exceeds 24, hydrophobicity of the acyl group part becomes too strong. [0007]

With regard to a process for producing the glycerin polyalkylene glycol ether derivative of the invention represented by the general formula [1], it can be particularly preferably produced by the method mentioned below.

(1) An alkylene oxide A^2O having 2 to 4 carbon atoms is added to a cyclic acetal or a cyclic ketal such as α, β -alkylidene glycerin, e.g., isopropylidene glycerin in an amount of 1 to 200 mol per mol of isopropylidene glycerin to synthesize an isopropylidene glycerin monopolyalkylene glycol ether. Then, after the terminal hydroxyl group is etherified with an alkyl chloride or the like or esterified with acetic anhydride or the like, the protective group forming the cyclic ketal structure is eliminated under an acidic condition, an alkylene oxide A^1O different from the first addition reaction is added in

an amount of 2 to 400 mol per mol of the resulting glycerin monopolyalkylene glycol ether derivative having two hydroxyl groups, and, if necessary, the terminal hydroxyl group is etherified or esterified to obtain the aimed derivative. In the present process for production, each of the alkylene oxide A¹O and the alkylene oxide A²O may be one alkylene oxide or two or more alkylene oxides. The reaction pathway of the present process for production is represented by the following formula [2].

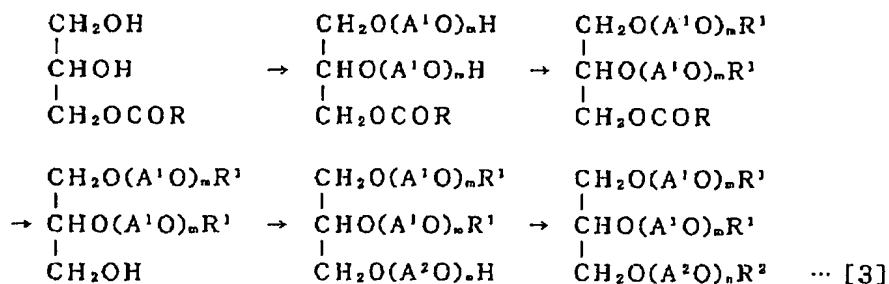


wherein A¹O and A²O are each an oxyalkylene group having 2 to 4 carbon atoms; (A¹O)_m and (A²O)_n are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products thereof; (A¹O)_m and (A²O)_n are different in structure from each other; R¹ and R² are each a hydrogen atom or a hydrocarbon group or acyl group having 1 to 24 carbon atoms and may be the same or different; m and n mean each an added mole number of an alkylene oxide; m is from 1 to

200; and m is from 1 to 200.

[0008]

(2) An alkylene oxide A¹O having 2 to 4 carbon atoms is added to a glycerin- α -monoester, e.g., glyceryl monoacetate in an amount of 2 to 400 mol per mol of glyceryl monoacetate to synthesize a glyceryl monoacetate dipolyalkylene glycol ether. Then, after the terminal two hydroxyl groups are, if necessary, etherified with an alkyl chloride, an alkylene oxide A²O different from the first addition reaction is added in an amount of 1 to 200 mol per mol of the glycerin dipolyalkylene glycol ether derivative having one hydroxyl group obtained by deacylation of the acyl group at α -position under an acidic condition, and, if necessary, the terminal hydroxyl group is etherified or esterified to obtain the aimed derivative. In the present process for production, each of the alkylene oxide A¹O and the alkylene oxide A²O may be one alkylene oxide or two or more alkylene oxides. The reaction pathway of the present process for production is represented by the following formula [3].



wherein A^1O and A^2O are each an oxyalkylene group having 2 to 4 carbon atoms; $(A^1O)_m$ and $(A^2O)_n$ are each a group consisting of one of addition products of an alkylene oxide having 2 to 4 carbon atoms or a group consisting of two or more of random-form or block-form addition products thereof; $(A^1O)_m$ and $(A^2O)_n$ are different in structure from each other; R^1 and R^2 are each a hydrogen atom or a hydrocarbon group or acyl group having 1 to 24 carbon atoms and may be the same or different; m and n mean each an added mole number of an alkylene oxide; m is from 1 to 200; and n is from 1 to 200.

[0009]

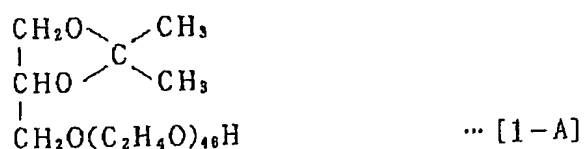
[Examples]

The following will describe the present invention in further detail with reference to Examples but the invention is by no means limited by these Examples. Incidentally, in Examples, pressure is represented by kg/cm^2 and % means wt%.

Example 1

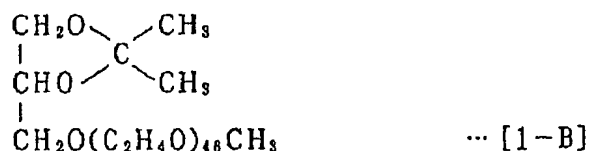
Into a 5 liter-volume autoclave were placed 158.4 g (1.2 mol) of isopropylidene glycerin and 2.4 g of sodium hydroxide. The atmosphere of the system was substituted with nitrogen gas, followed by temperature elevation to 100°C . Then, 2460 g (55.9 mol) of ethylene oxide was added under conditions of 100 to 150°C and 10 kg/cm^2 or lower

over the period of 4 hours, followed by continuation of reaction for further 1 hour. Then, while nitrogen gas was allowed to pass through to remove unreacted ethylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 2417 g of Compound 1-A. The hydroxyl value of the resulting compound was 26.6 (calculated value: 26.0 when 46 mol of ethylene oxide was added) and the freezing point was 49.7°C. From these results, the structure of Compound 1-A was deduced to be the formula [1-A].



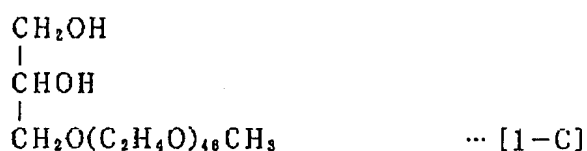
Then, into a 5 liter-volume autoclave were placed 2109 g (1 mol) of Compound 1-A and 84.5 g (1.56 mol) of sodium methoxide. After the atmosphere of the system was substituted with nitrogen gas, temperature was elevated to 100°C under stirring and sodium alkoxidation was conducted under 100 mmHg or lower for 1 hour. Then, the atmosphere of the system was returned to normal pressure with nitrogen gas and methyl chloride was blown therein. While

the blowing amount was controlled so that the atmosphere of the system became 1 kg/cm², the whole was maintained at 100°C for 3 hours. Then, while nitrogen gas was allowed to pass through, the whole was cooled to 60°C and also excessive methyl chloride was removed by evaporation. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 1930 g of Compound 1-B. The hydroxyl value of the resulting compound was 0.1 (calculated value: 0) and the freezing point was 48.9°C. From these results, the structure of Compound 1-B was deduced to be the formula [1-B].



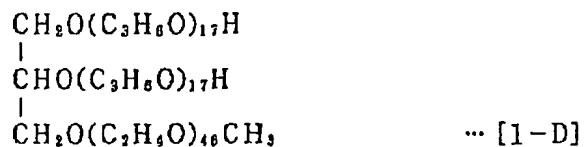
Then, 1900 g of Compound 1-B was placed in a 3 liter-volume glass reactor and pH was adjusted to 1.0 by addition of a 10% hydrochloride aqueous solution, followed by 1 hour of stirring at 60°C. Thereafter, pH of the reaction mixture was adjusted to 6.5 with a 50% sodium hydroxide aqueous solution and acetone formed was removed by evaporation together with water by heating at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction

mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 1684 g of Compound 1-C. The hydroxyl value of the resulting compound was 53.4 (calculated value: 52.7) and the freezing point was 49.4°C. From these results, the structure of Compound 1-C was deduced to be the formula [1-C].



Then, into a 5 liter-volume autoclave were placed 1050.5 g (0.5 mol) of 1-C and 4.0 g of sodium hydroxide. After the atmosphere of the system was substituted with nitrogen gas, 1050 g (18.1 mol) of propylene oxide was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 5 hours, followed by continuation of reaction for further 2 hours. Then, while nitrogen gas was allowed to pass through to remove unreacted propylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 1845 g of Compound 1-D. The hydroxyl value of the resulting compound was 28.2 (calculated value: 27.4) and the

freezing point was 41.2°C. From these results, the structure of Compound 1-D was deduced to be the formula [1-D].



Results of Example 1 are shown in Table 1.

[0010]

[Table 1]

Table 1

Symbol	Raw material product	Analytical value		
		Hydroxyl value (mgKOH/g)	Freezing point (°C)	Added mole number
1)	$ \begin{array}{c} \text{CH}_2\text{O} \diagup \text{C} \diagdown \text{CH}_3 \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{CH}_3 \\ \\ \text{CH}_2\text{OH} \end{array} $	425.0	0 or lower	α -position: 0 mol β -position: 0 mol γ -position: 0 mol
1-A	$ \begin{array}{c} \text{CH}_2\text{O} \diagup \text{C} \diagdown \text{CH}_3 \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{CH}_3 \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_5\text{O})_{46}\text{H} \end{array} $	26.6	49.7	α -position: 0 mol β -position: 0 mol γ -position: 46 mol EO
1-B	$ \begin{array}{c} \text{CH}_2\text{O} \diagup \text{C} \diagdown \text{CH}_3 \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{CH}_3 \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_5\text{O})_{46}\text{CH}_3 \end{array} $	0.1	48.9	α -position: 0 mol β -position: 0 mol γ -position: 46 mol EO
1-C	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_5\text{O})_{46}\text{CH}_3 \end{array} $	53.4	49.4	α -position: 0 mol β -position: 0 mol γ -position: 46 mol EO

1-D	$ \begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{17}\text{H} \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_{17}\text{H} \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{46}\text{CH}_3 \end{array} $	28.2	41.2	α -position: 17 mol PO β -position: 17 mol PO γ -position: 46 mol EO
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Note 1): isopropylidene glycerin

EO: ethylene oxide

PO: propylene oxide

[0011]

A gel permeation chromatogram of the resulting Compound 1-D is shown in Fig. 1 and an infrared absorption spectrum thereof is shown in Fig. 2. Measuring conditions of gel permeation chromatography are as follows.

<Measuring conditions of gel permeation chromatography>

Apparatus; SHODEX GPC SYSTEM-11

Developing solvent; tetrahydrofuran

Sample; 0.15% x 100 x 0.001 ml

Flow rate; 1.0 ml/min

Packed column: SHODEX KF-801, KF-803, KF-804

Column temperature: 40°C

Column length; I.D. 8 mm x 30 cm x 3

Detector; RI x 8

Measured results by gel permeation chromatography are as follows.

Number-average molecular weight (Mn) = 3967

Weight-average molecular weight (Mw) = 4118

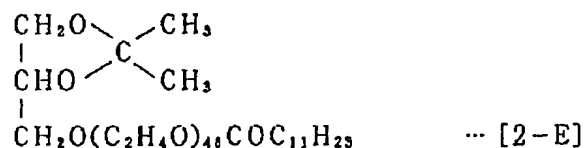
Polydispersity (M_w/M_n) = 1.038

Measured results of infrared spectroscopy are as follows. Absorption due to the hydroxyl group is observed at 3480 cm^{-1} . Absorption due to the methyl group and the methylene group are observed at 2870 cm^{-1} . Absorption due to the branched methyl group is observed at 1375 cm^{-1} and 1350 cm^{-1} . Absorption due to the ether bond is observed at 1120 cm^{-1} .

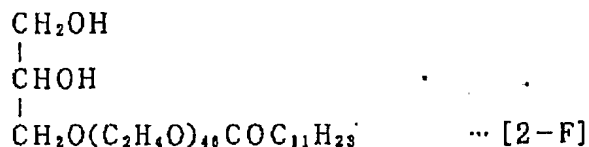
Example 2

Into a 2 liter-volume glass reactor were placed 1054.5 g (0.5 mol) of Compound 1-A and 42.1 g (0.78 mol) of sodium methoxide. Temperature was elevated to 100°C under stirring and sodium alkoxidation was conducted under 100 mmHg or lower for 1 hour. Then, the atmosphere of the system was returned to normal pressure with nitrogen gas and 174.8 g (0.8 mol) of lauroyl chloride was added dropwise over the period of 2 hours under a nitrogen atmosphere, followed by further 8 hours of reaction. After the reaction, the whole was cooled to 60°C , pH was adjusted to 7.0 with acetic acid, and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Thereafter, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 896 g of Compound 2-E. The hydroxyl value of the resulting Compound 2-E was 0.15 (calculated value: 0), the

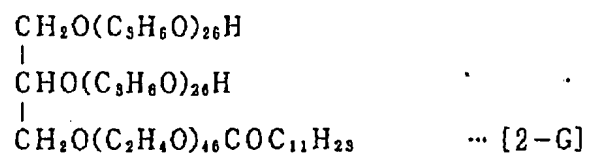
saponification value was 23.6 (calculated value: 24.0), and the freezing point was 45.7°C. From these results, the structure of Compound 2-E was deduced to be the formula [2-E].



Then, 700 g of Compound 2-E and 200 g of an 80% acetic acid aqueous solution were placed in a 1 liter-volume glass reactor and the whole was refluxed at 96°C for 3 hours. Thereafter, pH of the reaction mixture was adjusted to 6.5 with a 50% sodium hydroxide aqueous solution, and acetone formed was removed by evaporation together with water by heating at 100°C under 100 mmHg or lower for 1 hour. Then, the residue was cooled to 80°C and the precipitated salt was filtrated off to obtain 525 g of Compound 2-F. The hydroxyl value of the resulting Compound 2-F was 49.5 (calculated value: 48.8), the saponification value was 22.9 (calculated value: 24.4), and the freezing point was 46.2°C. From these results, the structure of Compound 2-F was deduced to be the formula [2-F].



Then, into a 5 liter-volume autoclave were placed 459.6 g (0.2 mol) of Compound 2-F and 2.0 g of sodium hydroxide. After the atmosphere of the system was substituted with nitrogen gas, temperature was elevated to 100°C and 609 g (10.5 mol) of propylene oxide was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 7 hours, followed by continuation of reaction for further 2 hours. Then, while nitrogen gas was allowed to pass through to remove unreacted propylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 962 g of Compound 2-G. The hydroxyl value of the resulting Compound 2-G was 22.1 (calculated value: 21.1), the saponification value was 29.8 (calculated value: 31.7), and the freezing point was 38.8°C. From these results, the structure of Compound 2-G was deduced to be the formula [2-G].



Results of Example 2 are shown in Table 2.

[0012]

[Table 2]

Table 2

Symbol	Raw material product	Analytical value			
		Hydroxyl value (mgKOH/g)	Saponification value (mgKOH/g)	Freezing point (°C)	Added mole number
2-E	$ \begin{array}{c} \text{CH}_2\text{O} \quad \diagdown \quad \text{CH}_2 \\ \quad \quad \diagup \quad \text{C} \\ \text{CHO} \quad \quad \diagdown \quad \text{CH}_3 \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{46}\text{COC}_{11}\text{H}_{23} \end{array} $	0.15	23.6	45.7	α -position: 0 mol β -position: 0 mol γ -position: 46 mol EO
2-F	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{46}\text{COC}_{11}\text{H}_{23} \end{array} $	49.5	22.9	46.2	α -position: 0 mol β -position: 0 mol γ -position: 46 mol EO
2-G	$ \begin{array}{c} \text{CH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_{26}\text{H} \\ \\ \text{CHO}(\text{C}_3\text{H}_6\text{O})_{26}\text{H} \\ \\ \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{46}\text{COC}_{11}\text{H}_{23} \end{array} $	22.1	29.8	38.8	α -position: 26 mol PO β -position: 26 mol PO γ -position: 46 mol EO

Note EO: ethylene oxide

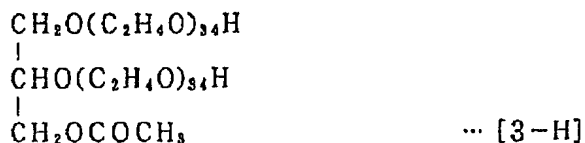
PO: propylene oxide

[0013]

Example 3

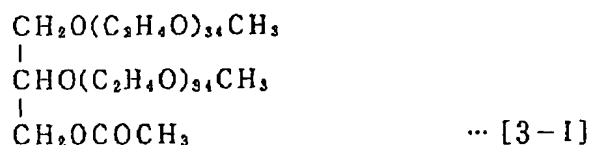
Into a 5 liter-volume autoclave were placed 134 g (1 mol) of glyceryl monoacetate and 3.0 g of sodium hydroxide. The atmosphere of the system was substituted with nitrogen gas, followed by temperature elevation to 100°C. Then, 3080 g (70 mol) of ethylene oxide was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 4 hours, followed by continuation of reaction for further 1 hour. Then, while nitrogen gas was allowed

to pass through to remove unreacted ethylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 3034 g of Compound 3-H. The hydroxyl value of the resulting Compound 3-H was 36.5 (calculated value: 35.9), the saponification value was 17.5 (calculated value: 17.9), and the freezing point was 47.3°C. From these results, the structure of Compound 3-H was deduced to be the formula [3-H].



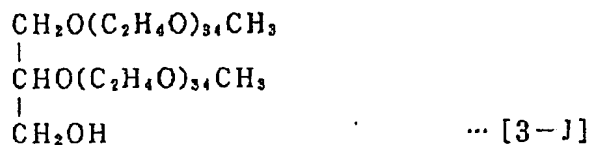
Then, into a 5 liter-volume autoclave were charged 2920 g (0.95 mol) of Compound 3-H and 169.0 g (3.12 mol) of sodium methyllate. After the atmosphere of the system was substituted with nitrogen gas, temperature was elevated to 100°C under stirring and sodium alkoxidation was conducted under 100 mmHg or lower for 1 hour. Then, the atmosphere of the system was returned to normal pressure with nitrogen gas and methyl chloride was blown therein. While the blowing amount was controlled so that the atmosphere of the system became 1 kg/cm², the whole

was maintained at 100°C for 3 hours. Then, while nitrogen gas was allowed to pass through, the whole was cooled to 60°C and also excessive methyl chloride was removed by evaporation. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 2739 g of Compound 3-I. The hydroxyl value of the resulting Compound 3-I was 0.1 (calculated value: 0), the saponification value was 16.9 (calculated value: 17.8), and the freezing point was 46.2°C. From these results, the structure of Compound 3-I was deduced to be the formula [3-I].



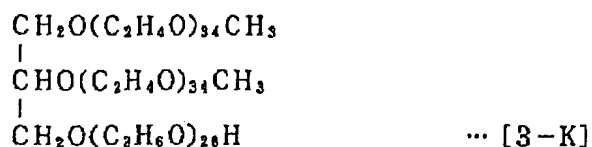
Then, 2600 g of Compound 3-I was placed in a 5 liter-volume glass reactor, and 100 g of a 30% sodium hydroxide aqueous solution was added thereto, followed by 1 hour of stirring at 80°C. Thereafter, pH was adjusted to 6.5 with a 10% hydrochloride aqueous solution and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the precipitated salt was filtrated off to obtain 2340 g of Compound 3-J. The hydroxyl value of

the resulting Compound 3-J was 18.7 (calculated value: 18.0), the saponification value was 0 (calculated value: 0), and the freezing point was 46.5°C. From these results, the structure of Compound 3-J was deduced to be the formula [3-J].



Then, into a 5 liter-volume autoclave were placed 2180 g (0.7 mol) of Compound 3-J and 4.0 g of sodium hydroxide. After the atmosphere of the system was substituted with nitrogen gas and then temperature was elevated to 100°C, 1100 g (19 mol) of propylene oxide was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 7 hours, followed by continuation of reaction for further 2 hours. Then, while nitrogen gas was allowed to pass through to remove unreacted propylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 2785 g of Compound 3-K. The hydroxyl value of the resulting Compound 3-K was 12.8 (calculated value: 12.1), the

saponification value was 0 (calculated value: 0), and the freezing point was 35.4°C. From these results, the structure of Compound 3-K was deduced to be the formula [3-K].



Results of Example 3 are shown in Table 3.

[0014]

[Table 3]

Table 3

Symbol	Raw material product	Analytical value			
		Hydroxyl value (mgKOH/g)	Saponification value (mgKOH/g)	Freezing point (°C)	Added mole number
2)	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{OCOCH}_3 \end{array} $	837	419	0 or lower	α -position: 0 mol β -position: 0 mol γ -position: 0 mol
3-H	$ \begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{34}\text{H} \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_{34}\text{H} \\ \\ \text{CH}_2\text{OCOCH}_3 \end{array} $	36.5	17.5	47.3	α -position: 34 mol EO β -position: 34 mol EO γ -position: 0 mol
3-I	$ \begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CH}_2\text{OCOCH}_3 \end{array} $	0.1	16.9	46.2	α -position: 34 mol EO β -position: 34 mol EO γ -position: 0 mol
3-J	$ \begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CH}_2\text{OH} \end{array} $	18.7	0	46.5	α -position: 34 mol EO β -position: 34 mol EO γ -position: 0 mol

3-K	$\begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_{34}\text{CH}_3 \\ \\ \text{CH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_{28}\text{H} \end{array}$	12.8	0	35.4	α -position: 34 mol EO β -position: 34 mol EO γ -position: 26 mol PO
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Note 2): glyceryl monoacetate

EO: ethylene oxide

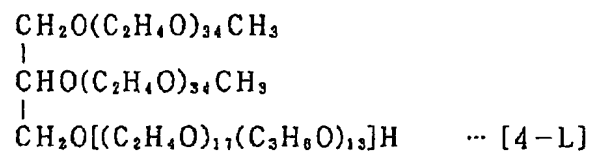
PO: propylene oxide

[0015]

Example 4

Into a 5 liter-volume autoclave were placed 2180 g (0.7 mol) of Compound 3-J and 4.0 g of sodium hydroxide. After the atmosphere of the system was substituted with nitrogen gas, temperature was elevated to 100°C. A mixture of 550 g (12.5 mol) of ethylene oxide and 550 g (9.5 mol) of propylene oxide mixed beforehand was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 5 hours, followed by continuation of reaction for further 2 hours. Then, while nitrogen gas was allowed to pass through to remove unreacted ethylene oxide and propylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the precipitated salt was filtrated off to obtain 2714 g of Compound 4-L. The hydroxyl value of the resulting Compound 4-L was 13.1 (calculated value: 12.2) and the

freezing point was 38.2°C. From these results, the structure of Compound 4-L was deduced to be the formula [4-L].



Results of Example 4 are shown in Table 4.

[0016]

[Table 4]

Table 4

Symbol	Raw material product	Analytical value		
		Hydroxyl value (mgKOH/g)	Freezing point (°C)	Added mole number
4-L	$\begin{array}{c} \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{CH}_3 \\ \\ \text{CHO}(\text{C}_2\text{H}_4\text{O})_4\text{CH}_3 \\ \\ \text{CH}_2\text{O}[(\text{C}_2\text{H}_4\text{O})_{17}(\text{C}_3\text{H}_6\text{O})_{13}]\text{CH}_3 \end{array}$	13.1	38.2	α -position: 34 mol PO β -position: 34 mol PO γ -position: 17 mol EO 13 mol PO

Note EO: ethylene oxide

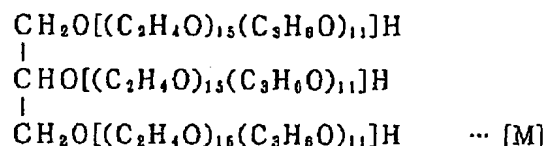
PO: propylene oxide

[0017]

Comparative Example 1

Into a 5 liter-volume autoclave were placed 69.0 g (0.75 mol) of glycerin and 4.0 g of sodium hydroxide. After the atmosphere of the system was substituted with nitrogen gas, temperature was elevated to 100°C. A mixture of 1500 g (34.1 mol) of ethylene oxide and 1500 g (25.9 mol) of propylene oxide mixed beforehand was added under conditions of 100 to 150°C and 10 kg/cm² or lower over the period of 5 hours, followed by continuation of reaction for further 2 hours. Then, while nitrogen gas was allowed to pass through to remove unreacted ethylene oxide and propylene oxide, the whole was cooled to 60°C. Thereafter, pH was adjusted to 7.0 with acetic acid and dehydration was conducted at 100°C under 100 mmHg or lower for 1 hour. Then, the reaction mixture was cooled to 80°C and the

precipitated salt was filtrated off to obtain 2701 g of Compound M. The hydroxyl value of the resulting Compound M was 41.9 (calculated value: 41.1) and the pour point was -34°C. From these results, the structure of Compound M was deduced to be the formula [M].



Results of Comparative Example 1 are shown in Table

5.

[0018]

[Table 5]

Table 5

Symbol	Raw material·product	Analytical value		
		Hydroxyl value (mgKOH/g)	Pour point (°C)	Added mole number
M	$\begin{array}{l} \text{CH}_2\text{O}[(\text{C}_2\text{H}_4\text{O})_{15}(\text{C}_3\text{H}_6\text{O})_{11}]\text{H} \\ \\ \text{CHO}[(\text{C}_2\text{H}_4\text{O})_{15}(\text{C}_3\text{H}_6\text{O})_{11}]\text{H} \\ \\ \text{CH}_2\text{O}[(\text{C}_2\text{H}_4\text{O})_{15}(\text{C}_3\text{H}_6\text{O})_{11}]\text{H} \end{array}$	41.9	-34	α -, β -, & γ - positions 15 mol EO 11 mol PO

Note EO: ethylene oxide

PO: propylene oxide

[0019]

Comparison in surface tension, freezing point, and cloud point between Compound 1-D of Example 1 and Compound M is shown in Table 6.

[0020]

[Table 6]

Table 6

		Compound 1-D	Comparative Example M
Surface tension (dyne/cm)	0.1% aqueous solution	35.0	38.6
	1.0% aqueous solution	35.4	40.0
Freezing point (°C)		41.2	-10 or lower
Cloud point (°C)		77.3	49.8

[0021]

Incidentally, the measuring methods are as follows.

Surface tension; Wilhelmy method, using Surface

Tentiometer A-3 [KYOWA KAGAKU Co. LTD]

Freezing point; in accordance with JIS K 0065

Cloud point; A 1 wt% aqueous solution of a sample is prepared, 7 ml of this solution is placed in a transparent glass tube having an inner diameter of 15 mm, a thermometer is inserted therein, the solution is heated under thorough stirring to a temperature about 2 to 3°C higher than the temperature at which clouding occurs, the solution is again air-cooled under thorough stirring, and temperature at which the solution becomes transparent is measured. From the above results, it is understood that the glycerin polyalkylene glycol ether derivative of the invention is different in physical properties from those having all the same polyoxyalkylene chains at α -, β -, and γ -positions.

[0022]

[Advantage of the Invention]

The present invention is a glycerin polyalkylene glycol ether derivative having polyoxyalkylene chains different in structure between α -, β -positions and γ -position of glycerin. The glycerin polyalkylene glycol ether derivative of the invention is different in physical properties from those having all the same polyalkylene chains at α -, β -, and γ -positions and can be utilized as a novel nonionic surfactant.

[Brief Description of the Drawings]

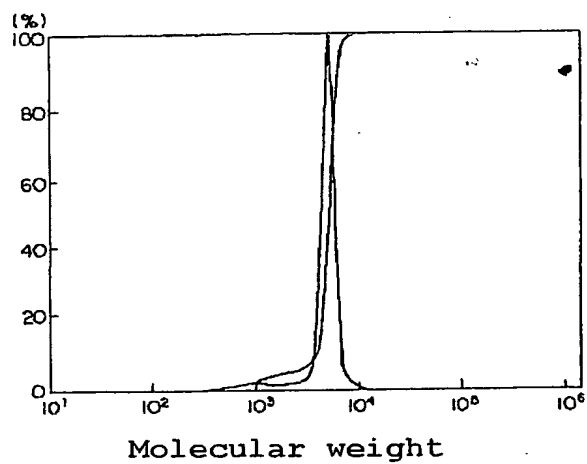
[Fig. 1]

Fig. 1 is a gel permeation chromatogram of Compound 1-D in Example 1.

[Fig. 2]

Fig. 2 is an infrared absorption spectrum of Compound 1-D in Example 1.

[Fig. 1]



[Fig. 2]

Transmittance (%)

